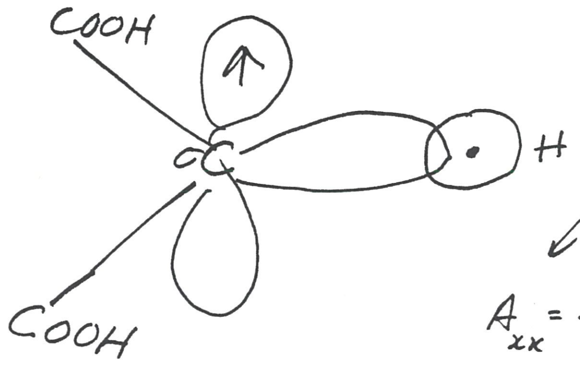
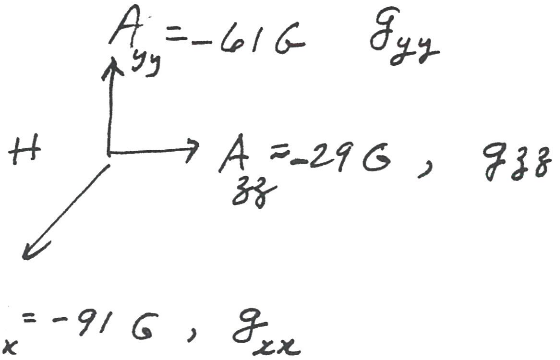
EPR Course
NTU
Fall 2001
Chan

November 28, 2001
Lecture 8

A second example to illustrate the usefulness of $\underset{\sim}{g}$ tensor and $\underset{\sim}{A}$ tensor in electron structure determination of an organic radical

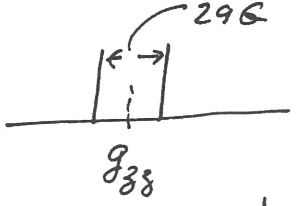
### Malonic acid radical





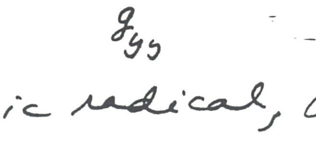
Obtained by γ-irradiation of Malonic acid crystals

When $\vec{H}$ aligned along z-axis, spectrum →



When $\vec{H}$ aligned along x-axis, spectrum →

When $\vec{H}$ aligned along y-axis, spectrum →

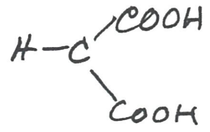


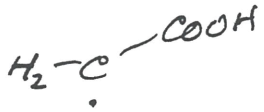
$g_{xx} \sim g_{yy} \sim g_{zz}$ typical for an organic radical, but

$|A_{xx}| > |A_{yy}| > |A_{zz}|$

Problem is actually more complicated, because there is another radical form$^{d}$ from γ-irradiation of malonic acid $\dot{C}H_2-COOH$, where the unpaired electron is coupled to 2 α-protons. So in practice, one must refer the EPR to the crystal axes $(\underline{a}, \underline{b}, \underline{c})$, and the molecular axes to $\underline{a}, \underline{b}, c$ through knowledge of crystal structure. But there are $\underline{2}$ radicals here. Nevertheless, can measure the resonance positions of all the signals as a function of $\underline{a}\,\underline{b}\,\underline{c}$ $\underline{\text{vis a}}$ $\underline{\text{vis}}$ $\vec{H}$. In principle, the resonances from the two radicals could be distinguished because they are of different intensities. Anyway, measurements yield

$$\begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{pmatrix} \qquad \underbrace{\begin{pmatrix} A'_{xx} & A'_{xy} & A'_{xz} \\ A'_{yx} & A'_{yy} & A'_{yz} \\ A'_{zx} & A'_{zy} & A'_{zz} \end{pmatrix} \quad \begin{pmatrix} A''_{xx} & A''_{xy} & A''_{xz} \\ A''_{yx} & A''_{yy} & A''_{yz} \\ A''_{zx} & A''_{zy} & A''_{zz} \end{pmatrix}}$$

for 
$H-\dot{C}(COOH)_2$

for 
$H_2-\dot{C}-COOH$

Suitable rotations of crystal axes $\underline{x}\,\underline{y}\,z$ will yield

$$\begin{pmatrix} A_{xx} & 0 & 0 \\ 0 & A_{yy} & 0 \\ 0 & 0 & A_{zz} \end{pmatrix} \qquad \begin{pmatrix} A'_{xx} & 0 & 0 \\ 0 & A'_{yy} & 0 \\ 0 & 0 & A'_{zz} \end{pmatrix} \qquad \begin{pmatrix} A''_{xx} & 0 & 0 \\ 0 & A''_{yy} & 0 \\ 0 & 0 & A''_{zz} \end{pmatrix}$$

but $\underline{\text{a}}$ $\underline{\text{different}}$ set of rotations for each $\underset{\sim}{A}$ $\underline{\text{matrix}}$

Return to <u>Malonic Acid Radical</u>

Only 1 $\alpha$-proton coupled to unpaired electron spin.

Two hyperfine lines only.

However, experiments do not yield the signs of A, B, C.

$$|A_{xx}| = |A| = 91\ G$$

$$|A_{yy}| = |B| = 61\ G$$

$$|A_{zz}| = |C| = 29\ G$$

Recall

$$A_{xx} = a + T_{xx}$$

$$A_{yy} = a + T_{yy}$$

$$A_{zz} = a + T_{zz}$$

and $T_{xx} + T_{yy} + T_{zz} = 0$

There are two possibilities:

$$a = +60.3\ MHz, \quad T_{zz} = -31.3\ MHz, \quad T_{xx} = +30.7\ MHz$$

$$T_{yy} = +0.7\ MHz$$

or

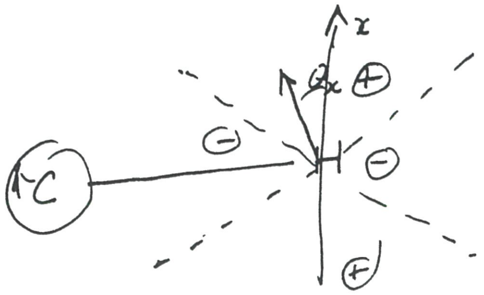
$$\boxed{\begin{array}{l} a = -60.3\ MHz, \quad T_{zz} = +31.3\ MHz, \quad T_{xx} = -30.7\ MHz \\ \qquad\qquad\qquad\qquad\qquad T_{yy} = -0.7\ MHz \end{array}}$$

<u>Expectations</u>

(1) $a < 0$ more likely for $\alpha$-proton coupled to an unpaired electron in $\pi$-orbital

(2) $$T_{xx} = -g_s g_N \beta \beta_N \left\langle \frac{R^2 - 3x^2}{R^5} \right\rangle$$

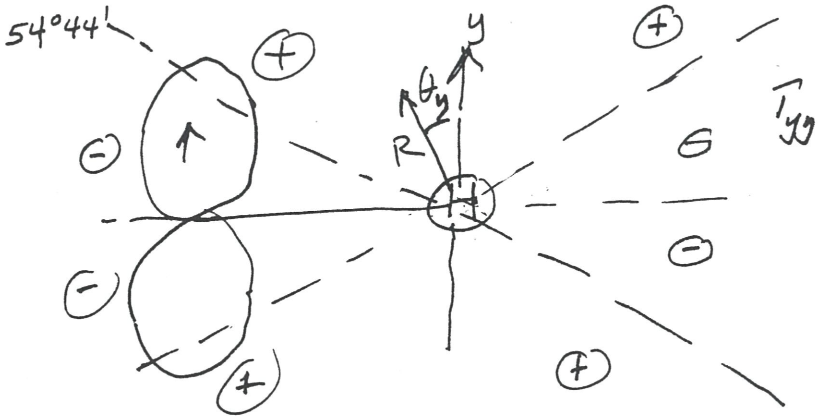
$$= g_s g_N \beta \beta_N \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \phi_c^* \phi_c \frac{3\cos^2\theta_x - 1}{R^3}\, d\varphi\, d\theta\, R^2 dR$$



$\phi_C^* \phi_C$ large only in region where $(3\cos^2\theta_x - 1) < 0$

∴ Integral $< 0$ or $T_{xx} < 0$ and large

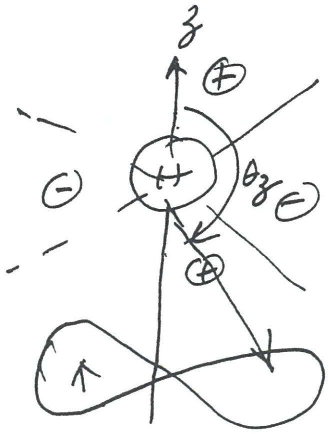
(3)



$$T_{yy} = +g_S g_N \beta\beta_N \cdot \int_0^\infty\int_0^\pi\int_0^{2\pi} \phi_C^* \phi_C \frac{(3\cos^2\theta_y - 1)}{R^3} \, d\varphi \, d\theta \, R^2 dR$$

~ small

(4)



$$T_{zz} = +g_S g_N \beta\beta_N \int_0^\infty\int_0^\pi\int_0^{2\pi} \phi_C^* \phi_C \frac{(3\cos^2\theta_z - 1)}{R^3} \, d\varphi \, d\theta \, R^2 dR$$ > 0 large

## Transition Metals

Differ from organic radicals in several respects.

(1) Spin-orbit interaction much larger.

(2) Unpaired electron(s) occupying ligand-field orbitals or MO's that are close together in energy.

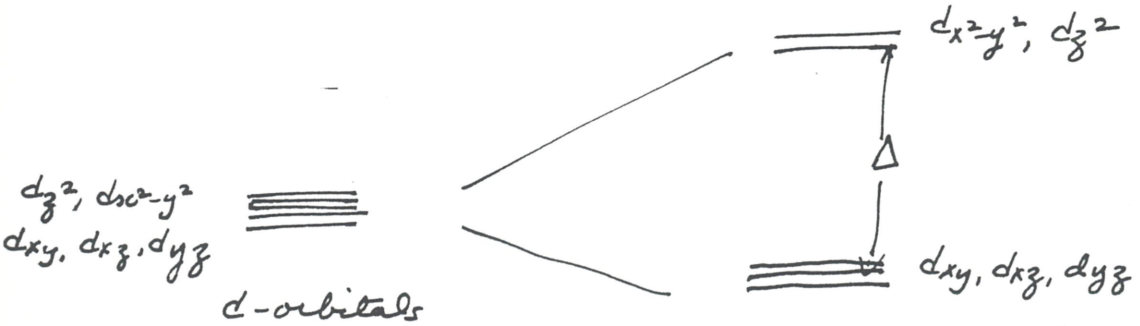
(3) Nuclear superhyperfine interactions in addition to nuclear hyperfine interaction

Nuclear superhyperfine interaction = coupling of unpaired electron to magnetic nuclei on ligands

Nuclear hyperfine interaction = coupling of unpaired electron to transition metal nucleus, if the latter is magnetic

Because of (1) and (2), $\Delta g$, that is, deviation of $g$ from free-electron spin value ($g_s = 2.0023$) is much larger for transition metal EPR compared with organic radicals.

Illustrate above ideas with a transition metal ion with $d^n$ electronic configuration

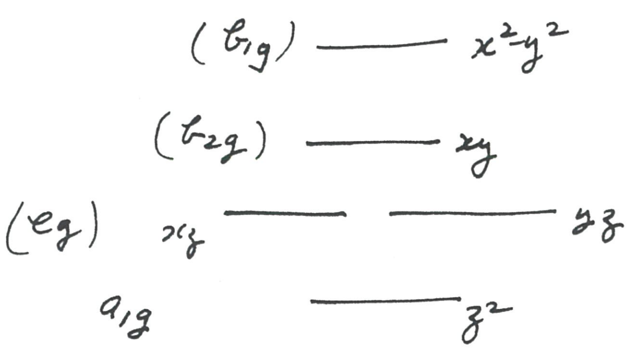


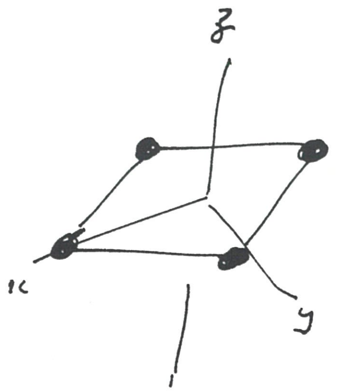
d-orbitals degenerate

"Isolated ion"

octahedral complex

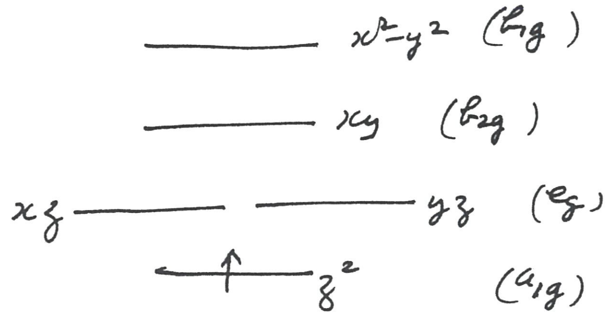
Ion in octahedral crystal field or ligand field.





Tetragonal crystal field
Tetragonal ligand field
Tetragonal complex

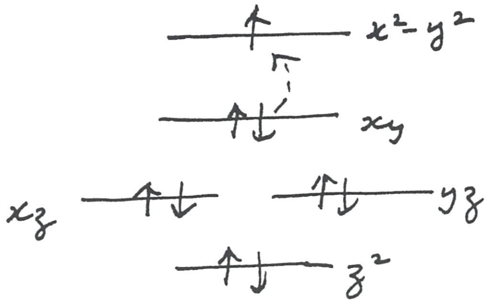
$\underline{d^1}$



$Ti^{3+}$

systems with 1 unpaired electron

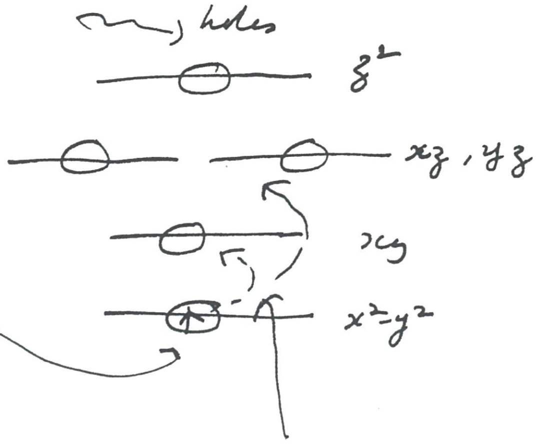
$\underline{d^9}$



$Cu^{2+}$

equivalent to one electron hole in the d-shell

hole diagram



system with 1 unpaired electron hole

d-d optical transitions correspond to excitations of the hole from 1 hole-state to another

If there is NOT much covalency, we may assume that the unpaired electron is <u>localized</u> on transition metal (crystal field limit). Otherwise, must take into account the delocalization of unpaired electron into ligands, or covalency effects. This is done two ways

① introducing orbital reduction factor at transition metal

② doing full fledged MO calculations.

$\boxed{\text{EPR}}$

$$\mathcal{H} = \underbrace{-\vec{H}\cdot\vec{\mu}_S - \vec{H}\cdot\vec{\mu}_L}_{\substack{\text{electron}\\ \text{Zeeman}}} + \underbrace{\lambda\vec{L}\cdot\vec{S}}_{\substack{\text{spin-}\\ \text{orbit}\\ \text{interaction}}} + \underbrace{\vec{S}\cdot\underset{\sim}{A}\cdot\vec{I}}_{\substack{\text{nuclear}\\ \text{hyperfine}\\ \text{interaction}}}$$

$$+ \underset{\substack{\text{ligand}\\ \text{magnetic}\\ \text{nuclei}}}{\sum_{N'} \vec{S}\cdot\underset{\sim}{A}_{N'}\cdot\vec{I}_{N'}} \qquad - \underset{\substack{\text{all}\\ \text{nuclei}\\ \\ \text{nuclear Zeeman}\\ \text{interaction}}}{\sum_{N} \vec{H}\cdot\vec{\mu}_N}$$

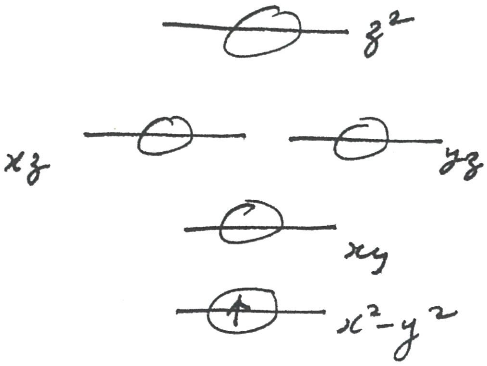
where $I$ is the nuclear spin of the transition metal ion;

$N'$ refers to magnetic nuclei associated with ligands, e.g. $^1H$, $^{14}N$, $^{13}C$, $^{15}N$, etc.

or

$$\underset{\substack{\text{Spin}\\ \text{Hamiltonian}}}{\mathcal{H}_S} = \underset{\substack{\text{electron}\\ \text{Zeeman}}}{+\vec{S}\cdot\underset{\sim}{g}\cdot\vec{H}} + \underset{\substack{\text{nuclear}\\ \text{hyperfine}}}{\vec{S}\cdot\underset{\sim}{A}\cdot\vec{I}} + \underset{\substack{\text{ligand magnetic}\\ \text{nuclei}}}{\sum_{N'} \vec{S}\cdot A_{N'}\cdot I_{N'}} - \underset{\substack{\text{all}\\ \text{nuclei}}}{\sum_{N} \vec{H}\cdot\vec{\mu}_N}$$

## Do g-value or tensor calculation for tetragonal $Cu^{2+}$



$d_{z^2} = d_0$

$d_{xz}, d_{yz} = \frac{1}{\sqrt{2}}(d_1 \pm d_{-1})$

$d_{xy} = \frac{1}{\sqrt{2}}(d_2 - d_{-2})$

$d_{x^2-y^2} = \frac{1}{\sqrt{2}}(d_2 + d_{-2})$

### Wavefunction for electron hole

$d_{x^2-y^2} \cdot \alpha$ (spin ↑)

$d_{x^2-y^2} \cdot \beta$ (spin ↓)

### d-orbitals

$$d_2 = \sqrt{\frac{15}{8\pi}} \cdot f(r) \cdot \left(\frac{1}{4}\sin^2\theta \cdot e^{2i\phi}\right)$$

$$d_1 = \sqrt{\frac{15}{8\pi}} \cdot f(r) \cdot \left(-\sin\theta\cos\theta \cdot e^{i\phi}\right)$$

$$d_0 = \sqrt{\frac{15}{8\pi}} \cdot f(r) \cdot \left(\frac{1}{\sqrt{6}}(3\cos^2\theta - 1)\right)$$

$$d_{-1} = \sqrt{\frac{15}{8\pi}} \cdot f(r) \cdot \left(+\sin\theta\cos\theta \cdot e^{-i\phi}\right)$$

$$d_{-2} = \sqrt{\frac{15}{8\pi}} \cdot f(r) \cdot \left(\frac{1}{4}\sin^2\theta \cdot e^{-2i\phi}\right)$$

Recall, according to perturbation theory,

$$\psi_+ = d_{x^2-y^2} \cdot \alpha - \sum_{\substack{i = xy,\\ yz, xz,\\ z^2\\ m_s = \pm\frac{1}{2}}} \frac{\int d_i^* \phi_{m_s}^* (\lambda \vec{L} \cdot \vec{S})\, d_{x^2-y^2} \cdot \alpha \, d\tau \, d\tau_s}{E(d_i \phi_{m_s}) - E(d_{x^2-y^2} \cdot \alpha)} \, d_i \cdot \phi_{m_s}$$

where $d_i$ refer to ith d-orbital

$\phi_{m_s}$ refers to approximate spin function $(\alpha, \beta)$

and

$$\psi_- = d_{x^2-y^2}\cdot\beta - \sum_{\substack{i=xy,\\ yz,xz,z^2\\ m_s=\pm\frac{1}{2}}} \frac{\int d_i^*\cdot\phi_{ms}^*\left(\lambda\vec{L}\cdot\vec{S}\right)d_{x^2-y^2}\cdot\beta\, d\tau\, d\xi}{E(d_i\cdot\phi_{ms}) - E(d_{x^2-y^2}\cdot\beta)}\, d_i\phi_{ms}$$

x, y, z refer to a set of molecular axes!

Since $\vec{L}\cdot\vec{S} = L_z S_z + L_x S_x + L_y S_y$

$= L_z S_z + \frac{1}{2}(L^+S^- + L^-S^+)$

$\hat{L}_z\hat{S}_z$ mixes in some $\underline{d_{xy}\cdot\alpha}$ with $d_{x^2-y^2}\cdot\alpha$

and some $\underline{d_{xy}\cdot\beta}$ with $d_{x^2-y^2}\cdot\beta$

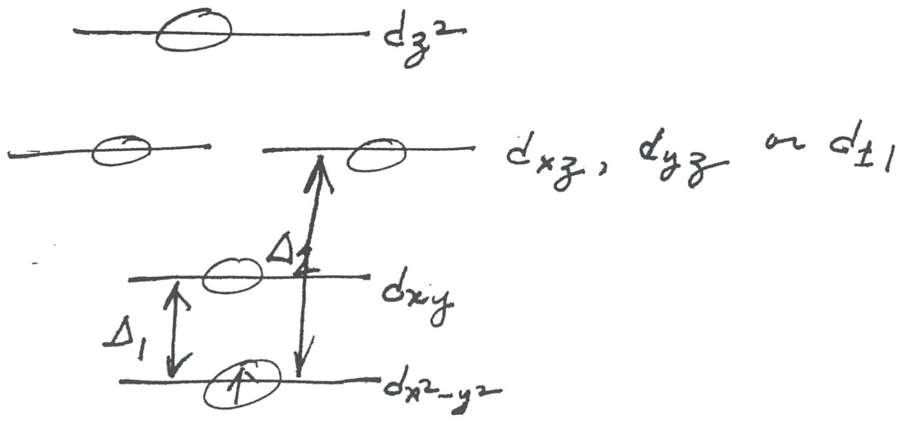
$L^+S^-$ mixes in some $d_{-1}\cdot\beta$ with $d_{x^2-y^2}\cdot\alpha$

$L^-S^+$ mixes in some $d_{+1}\cdot\beta$ with $d_{x^2-y^2}\cdot\alpha$

If we do algebra, we find

$$\psi_+ = d_{x^2-y^2}\cdot\alpha - \frac{\lambda}{\Delta_1}d_{xy}\cdot\alpha - \frac{1}{\sqrt{2}}\frac{\lambda}{\Delta_2}d_{-1}\cdot\beta$$

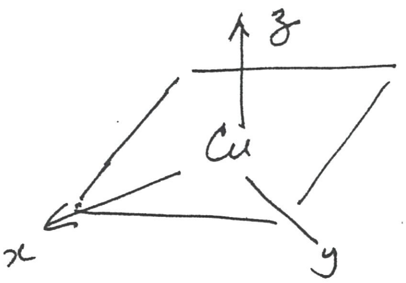
and $$\psi_- = d_{x^2-y^2}\cdot\beta + \frac{\lambda}{\Delta_1}d_{xy}\cdot\alpha - \frac{1}{\sqrt{2}}\frac{\lambda}{\Delta_2}d_{+1}\cdot\alpha$$



Now $\mathcal{H}_Z = +g_s \beta \vec{H}\cdot\vec{S} + g_L \beta \vec{H}\cdot\vec{L}$

$$= \beta \begin{pmatrix} H_x & H_y & H_z \end{pmatrix} \begin{pmatrix} g_s S_x + L_x \\ g_s S_y + L_y \\ g_s S_z + L_z \end{pmatrix}$$

Let's take magnetic field along z-direction



so that $H_x = 0$
$H_y = 0$

$$\mathcal{H}_Z = \beta H_z (g_s S_z + L_z) = \beta H_0 (g_s S_z + L_z)$$

Zeeman energy

$$= \int \psi_\pm^* \, \beta H_0 (g_s S_z + L_z)\, \psi_\pm \, d\tau \, d\tau_s$$

$$= \beta H_0 \left[ g_s \left(\pm \tfrac{1}{2}\right) \mp \frac{4\lambda}{\Delta_1} + \text{higher order terms} \right]$$

$$\cong \beta H_0 \left(\pm \tfrac{1}{2}\right) \underbrace{\left(g_s - \frac{8\lambda}{\Delta_1}\right)}_{g_{zz} \text{ or } g_{\parallel} \, = \, g_s \left(1 - \frac{4\lambda}{\Delta_1}\right)} = \beta H_0 g_{\parallel} \left(\pm \tfrac{1}{2}\right)$$

When magnetic field is along x-direction or y-direction

Say x  $\hat{\mathcal{H}}_Z = +g_s H_0 (g_s \hat{S}_x + \hat{L}_x)$

$$\hat{\mathcal{H}}_z = \left(\begin{array}{c|cc} & \psi_+ & \psi_- \\ \psi_+ & 0 & -\frac{\lambda}{\Delta_2} + g_s(\frac{1}{2}) \\ \psi_- & -\frac{\lambda}{\Delta_2} + g_s(\frac{1}{2}) & 0 \end{array}\right) \beta H_0$$

Degenerate situation

So correct $\psi_x^{\pm} = \frac{1}{\sqrt{2}}(\psi_+ \pm \psi_-)$

and Zeeman energies are (obtained by diagonalizing above 2×2 matrix)

$$= \pm \beta H_0 \left(g_s \tfrac{1}{2} - \frac{\lambda}{\Delta_2}\right)$$

$$= \pm \beta H_0 \left(\tfrac{1}{2}\right) \underbrace{\left(g_s - \frac{2\lambda}{\Delta_2}\right)}_{g_{xx}}$$

$g_{yy}$ (identical result when $H_0$ is along y axis)

$$g_\perp = g_s\left(1 - \frac{\lambda}{\Delta_2}\right)$$

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For $Cu^{2+}$

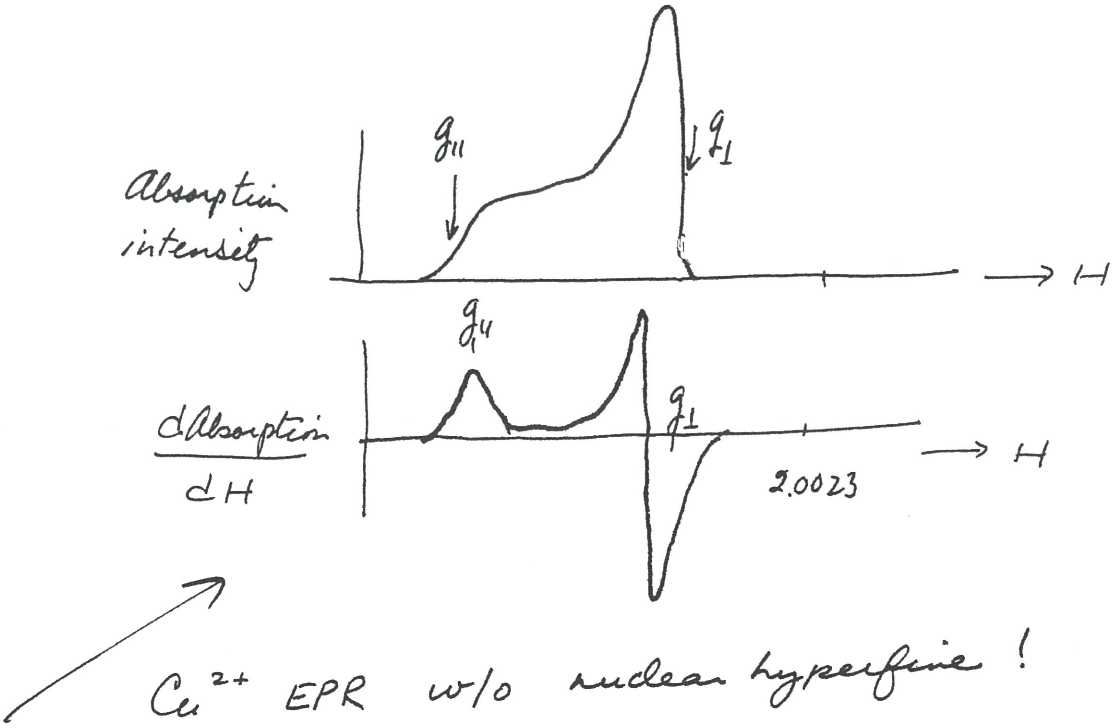
$\lambda = \ominus 829\ \text{cm}^{-1}$

$$g_{\parallel} = g_s\left(1 - \frac{4\lambda}{\Delta_1}\right) = g_s\left(1 + \frac{4|\lambda|}{\Delta_1}\right) > g_s$$

$$g_\perp = g_s\left(1 - \frac{\lambda}{\Delta_2}\right) = g_s\left(1 + \frac{|\lambda|}{\Delta_2}\right) > g_s$$

But $\Delta_2 >> \Delta_1$

$$\therefore \boxed{g_{\parallel} > g_\perp > g_s}$$



$Cu^{2+}$ EPR w/o nuclear hyperfine!

If unpaired electron was in $d_{z^2}$ orbital, e.g. $d^1$ or $Ti^{3+}$,

Then $g_s > g_\parallel, g_\perp$

and EPR will appear at g's below 2.0023!

To complete picture, let's now include

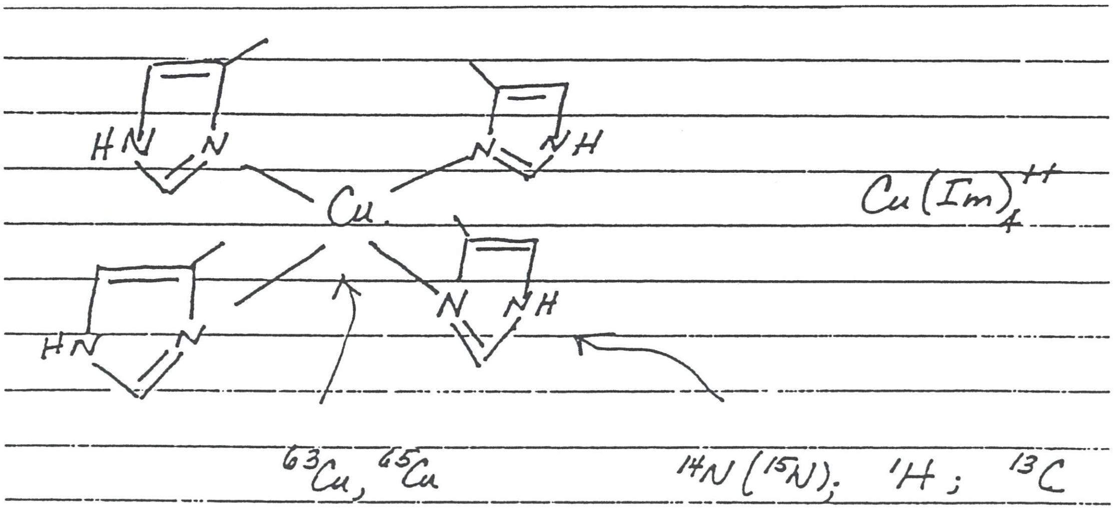
nuclear hyperfine interaction.

## Nuclear hyperfine interaction in EPR spectroscopy of transition metal complexes

Interaction of unpaired e$^-$ (or hole) with nuclear spin of transition metal ion and magnetic nuclei of ligands

$$\underbrace{\bar{S}\cdot\mathbf{A}\cdot I}_{\substack{\text{nuclear}\\\text{hyperfine}\\\text{interaction}}}+\underbrace{\sum_{N'}\bar{S}\cdot\mathbf{A}_{N'}\cdot I_{N'}}_{\substack{\text{magnetic}\\\text{nuclei on}\\\text{ligands}\\ \\\text{nuclear}\\\text{superhyperfine}\\\text{interaction}}}-\underbrace{\sum_{N'}\vec{H}\cdot\vec{\mu}_N}_{\substack{\text{all}\\\text{magnetic}\\\text{nuclei}\\ \\\text{nuclear}\\\text{Zeeman}\\\text{interaction}}}$$

Example



$$\underbrace{I=3/2}_{}$$

Coupling of electron hole or spin to Cu nucleus
→ nuclear hyperfine interaction

$$I=1 \quad \underbrace{I=1/2;\quad I=1/2;\ I=1/2}_{}$$

coupling of electron hole or spin to ligand magnetic nuclei
→superhyperfine interaction

Focus on nuclear hyperfine interaction

$$\vec{S}\cdot\mathbf{A}\cdot\vec{I} - \vec{\mu}_N\cdot\vec{H}$$

Since $\vec{\mu}_N = g_I\beta_N\vec{I}$ , where $g_I$ = nuclear g-value

$\beta_N$ = nuclear Bohr magneton = $\dfrac{e\hbar}{2M_\rho c}$

Can rewrite as

$$\vec{S}\cdot\mathbf{A}\cdot\vec{I} - g_I\beta_N\vec{H}\cdot\vec{I} = -g_I\beta_N\left(\vec{H}_e + \vec{H}\right)\cdot\vec{I}$$

where $g_I\beta_N\vec{H}_e = -\vec{S}\cdot\mathbf{A}$

or $g_I\beta_N\begin{pmatrix} H_{ex} & H_{ey} & H_{ez}\end{pmatrix} = -\begin{pmatrix} S_x & S_y & S_z\end{pmatrix}\begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz}\end{pmatrix}$

can refer to $\vec{H}e$ as the magnetic field produced by spinning electron at transition metal nucleus.

Pick symmetric $D_{4h}$ complex

$\mathbf{A}$ = "A " tensor or nuclei hyperfine tensor

$$= \begin{pmatrix} A_{xx} & 0 & 0 \\ 0 & A_{yy} & 0 \\ 0 & 0 & A_{zz}\end{pmatrix} = \begin{pmatrix} A_\perp & 0 & 0 \\ 0 & A_\perp & 0 \\ 0 & 0 & A_{\parallel}\end{pmatrix}$$

Then $g_I\beta_N\begin{pmatrix} H_{ex} & H_{ey} & H_{ez}\end{pmatrix} = \ominus\begin{pmatrix} S_xA_\perp & S_yA_\perp & S_zA_{\parallel}\end{pmatrix}$

So total magnetic field experienced by magnetic nucleus is given by

$$\left( H_x - \frac{A_\perp S_x}{g_I \beta_N}, H_y - \frac{A_{\perp'} S_y}{g_I \beta_N}, H_y - \frac{A_{\parallel} S_z}{g_I \beta_N} \right)$$

and the effective Hamiltonian for the problem because

$$\beta \begin{pmatrix} H_x & H_y & H_z \end{pmatrix} \begin{pmatrix} g_\perp & 0 & 0 \\ 0 & g_{\perp'} & 0 \\ 0 & 0 & g_{\parallel} \end{pmatrix} \begin{pmatrix} S_x \\ S_y \\ S_z \end{pmatrix} +$$

$$\begin{pmatrix} A_\perp S_x - g_I \beta_N H_x, A_{\perp'} S_y - g_I \beta_N H_y, A_{\parallel} S_z - g_I \beta_N H_z \end{pmatrix} \begin{pmatrix} I_x \\ I_y \\ I_z \end{pmatrix}$$

(1)<u>For applied magnetic field along z-axis</u>

$$H_x = 0, H_y = 0, H_z = H_o$$

$$\text{Hamiltonian} = \beta H_0 g_{\parallel} S_z + A_\perp S_x I_x + A_{\perp'} S_y I_y + A_{\parallel} S_z I_z - g_I \beta_N H_0 I_z$$

If $\bar{S}$ and $\bar{I}$ are both quantized along $\bar{H}$,

$$\therefore \langle S_z \rangle = \pm 1/2 \qquad \langle I_z \rangle = m_I$$

$$\langle S_x \rangle = 0 \qquad \langle I_x \rangle = 0$$

$$\langle S_y \rangle = 0 \qquad \langle I_y \rangle = 0$$

$$\text{Energy} = \beta H_0 g_{\parallel} m_S + A_{\parallel} m_S m_I - g_I \beta_N H_0 m_I$$

EPR Selection rule $\Delta m_S = \pm 1, \ \Delta m_I = 0$

$$\boxed{h\nu = \beta H_0 g_{\parallel} + A_{\parallel} m_I}$$

(2) For applied magnetic field along x-axis

$$H_x = H_0,\ H_y = 0,\ H_z = 0$$

$$\text{Hamiltonian} = \beta H_0 g_{\perp} S_x + A_{\perp} S_x I_x + A_{\perp'} S_y I_y + A_{\sqcap} S_z I_z - g_I \beta_N H_0 I_x$$

$$\text{Energy} \ = \ \beta H_0 g_{\perp} m_S + A_{\perp} m_S m_I - g_I \beta_N H_0 m_I$$

and EPR transition occur at

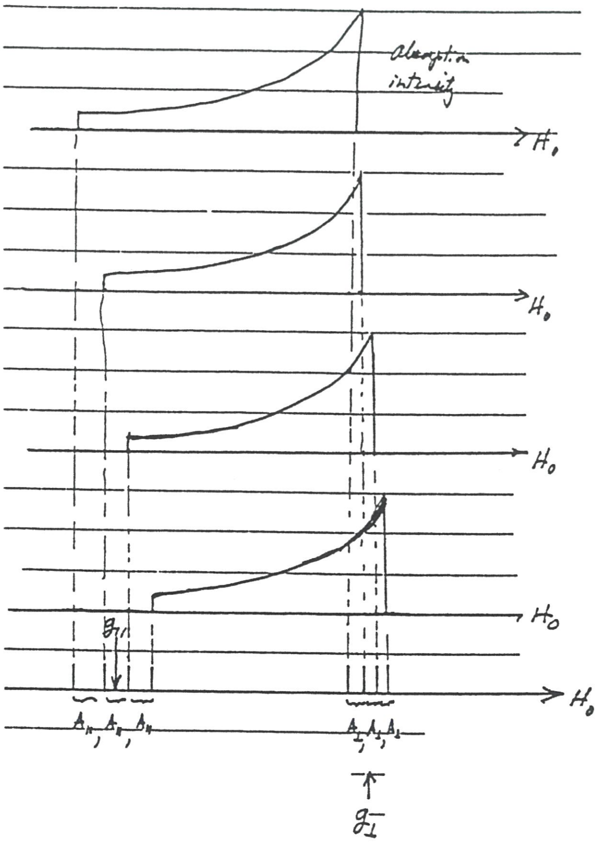
$$\boxed{h\nu = \beta H_0 g_{\perp} + A_{\perp} m_I}$$

Return to Cu (II) complexes

| | | | | $\gamma$ |
|---|---|---|---|---|
| 2 Cu isotopes: | $^{63}$Cu | 69.09% | I = 3/2 | 7.1088 |
| | $^{65}$Cu | 30.91% | I =3/2 | 7.6104 |

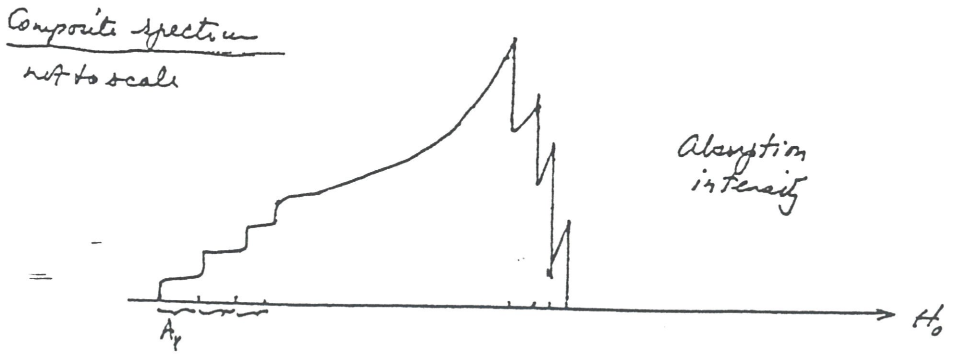
Therefore observed powder spectrum is a superposition of eight powder sub-spectra, one for each of the $m_I$'s for the two Cu isotopes. But $g_I$'s for the two Cu isotopes differ by $\overset{=}{<}$10%. So for all practical purposes, can interpret the observed spectrum as a superposition of four "power sub-spectra".

Expected spectrum sum of following 4 subspectras:



| | |
|---|---|
| $m_I$=-3/2 | $m_I$=+3/2 |
| $m_I$=-1/2 | $m_I$=+1/2 |
| $m_I$=+1/2 | $m_I$=-1/2 |
| $m_I$=+3/2 | $m_I$=-3/2 |
| $A_\parallel$, $A_\perp < 0$ | $A_\parallel$, $A_\perp > 0$ |

I have assumed that $A_\parallel$ and $A_\perp$ are of the same sign, but that need not by the case.



Experiments ( Data take from Solomon's review in Chem. Reviews )

Tetragonal Cu (II) or type 2 Cu (II)

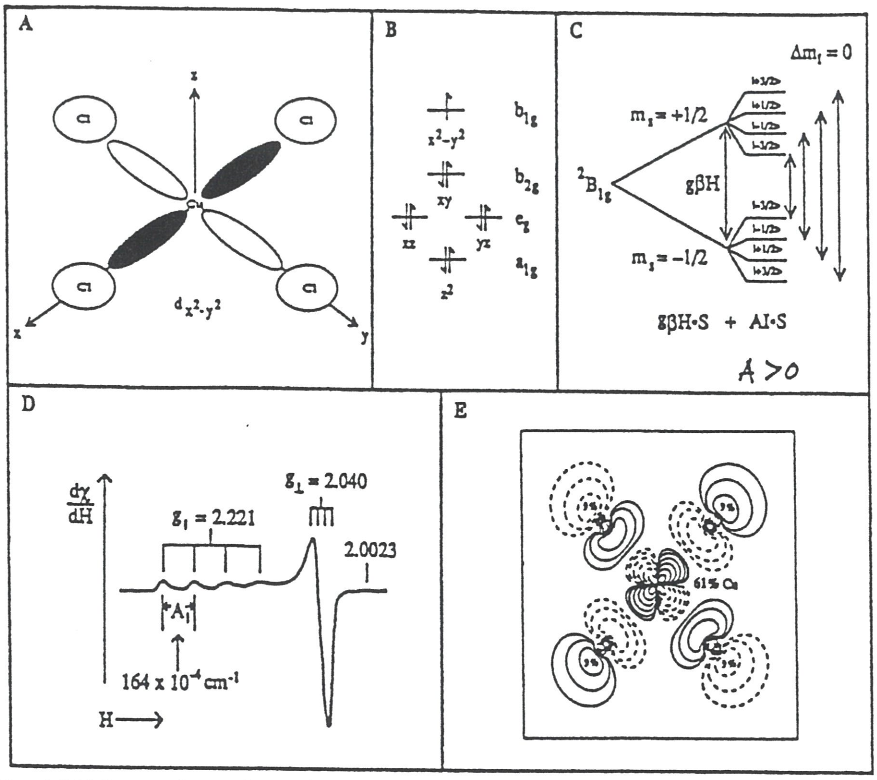


**Figure 1.** Ligand-field theory and ground-state electronic properties of normal cupric complexes: (A) square planar $D_{4h}$-$CuCl_4^{2-}$; (B) ligand field splitting of d orbitals in $D_{4h}$ symmetry; (C) $^2B_{1g}$ ground-state Zeeman and hyperfine splitting diagram; (D) powder pattern EPR spectrum of the $^2B_{1g}$ ground state; (E) $^2B_{1g}$ ground-state wave function from adjusted-sphere SCF-Xα-SW calculation.

Observed $g_\parallel = 2.221$, $g_\perp = 2.040$

Predicted

reduced g-values due to covalency

(a) ligand-field (no covalent delocalization of metal d-orbitals onto ligand valence orbitals

$g_\parallel = 2.743$, $g_\perp = 2.177$

(b) Self-consistent field $X_\alpha$ scattered wave (SCF- $X_\alpha$-SW)

$g_\parallel = 2.144$, $g_\perp = 2.034$

## Blue copper site

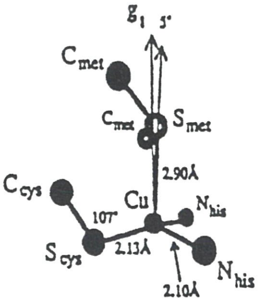


**Figure 4.** X-ray structure of the copper coordination environment of oxidized poplar plastocyanin at 1.6-Å resolution.[20] The $g_\parallel$ orientation was determined from single-crystal EPR spectroscopy.[25]

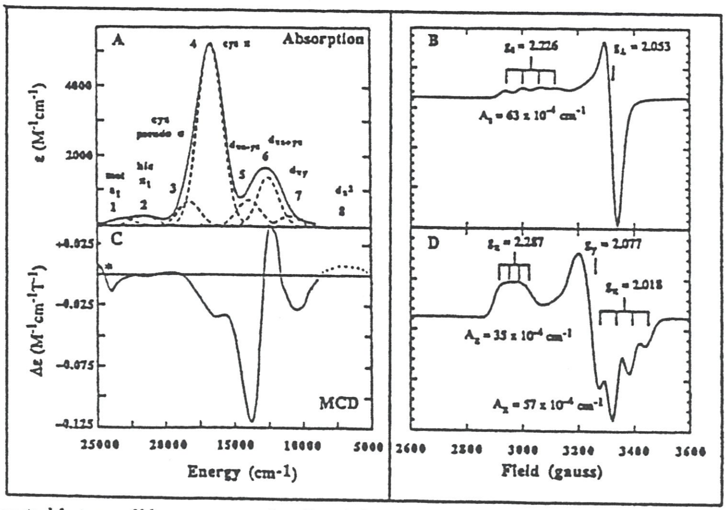


**Figure 3.** Unique spectral features of blue copper proteins: Part A shows the low-temperature (LT) absorption spectrum of plastocyanin. The dashed lines indicate Gaussian band deconvolution of the spectrum. Assignments of bands 1–8 were determined from LT-absorption and LT-MCD spectroscopies. Part B shows the EPR spectrum of spinach plastocyanin, and C, the LTMCD spectrum of spinach plastocyanin. The dotted portion of the spectrum is estimated from the NIR-LT-MCD spectrum of azurin (see ref 26). The feature marked with an asterisk (*) is due to a small amount of heme impurity. Part D shows the EPR spectrum of stellacyanin.

Observed (for blue copper site in plastocyanin)

$g_\parallel = 2.226$, $g_\perp = 2.053$

(for blue copper site in stellacyanin)

$g_z = 2.287$, $g_y = 2.077$ , $g_x = 2.018$

rhombic!

Understanding **A**. The nuclear hyperfine interaction

There are 2 contributions to **A**

a) Fermi-contact interaction (isotropic)

$$a\bar{I}\cdot\bar{S} \quad \text{where } a = \frac{8\pi}{3} g_S\beta g_I\beta_N|\varphi(0)|^2$$

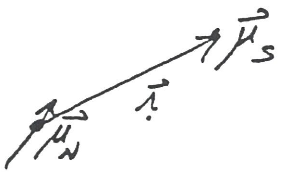
where $\varphi(0) \equiv$ value of wavefunction of unpaired electron at nucleus.

direct: S-electrons

indirect : spin polarization of inner S-shell such that $\varphi^{\alpha}_{ns}(0) \neq \varphi^{\beta}_{ns}(0)$

b) Magnetic dipolar interaction between unpaired electron spin and magnetic moment of nucleus.

$$\frac{\bar{\mu}_S\cdot\bar{\mu}_N}{r^3} - \frac{3(\bar{\mu}_S\cdot\bar{r})(\bar{r}\cdot\bar{\mu}_N)}{r^5} = -g_S\beta g_I\beta_N\left(\frac{\bar{I}\cdot\bar{S}}{r^3} - \frac{3(\bar{I}\cdot\bar{r})(\bar{r}\cdot\bar{S})}{r^5}\right)$$



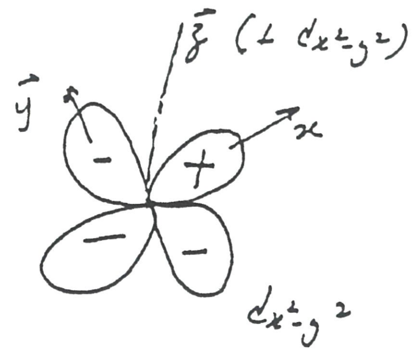
If expand dot-products using Cartesian coordinates x, y, z

$$= -g_S\beta g_I\beta_N\left\{S_xI_x\left\langle\frac{r^2-3x^2}{r^5}\right\rangle + S_yI_y\left\langle\frac{r^2-3y^2}{r^5}\right\rangle + S_zI_z\left\langle\frac{r^2-3z^2}{r^5}\right\rangle\right\}$$

Where < > denote averaging over the wavefunction describing the electron spin

$$= T_{xx}S_xI_x + T_{yy}S_yI_y + T_{zz}S_zI_z$$

For Cu (II) complex, with the unpaired $e^-$ in "$d_{x2-y2}$ "orbital



Simple to show that, in this case,

$$T_{xx} = T_{yy} = -\frac{1}{2}T_{zz}$$

and $T_{zz} < 0$ $\qquad \because \int \left(d_{x^2-y^2}\right)\left(\frac{r^2-3z^2}{r^5}\right)d_{x^2-y^2}d\tau > 0$

A turns out to be negative as well because unpaired $e^-$ is in $d_{x^2-y^2}$ orbital, which has a node at Cu nucleus. Only way for $a \neq 0$ is to have spin polarization of inner s-shells by $d_{x^2-y^2}$ electron.

Thus

$$A_{\parallel} = a + T_{zz} < 0$$

$$A_{\perp} = a + T_{xx} = a - \frac{1}{2}T_{zz} \approx 0$$

$$<0 \quad >0$$

$CuCl_4^{2-}$ : $\quad |A_{\parallel}| = 164\times10^{-4}\ cm^{-1}$

$= 164\times10^{-4}\times3\times10^{10}\,Hz$

$= 492MHz$

$= \frac{492}{2.8}$ Gauss = 175 Gauss ( $A_{\parallel}$ should be < 0)

$|A_{\perp}|$ small